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(54) Fracturing subterranean zones

(57) Subterranean zones are fractured using a fracturing fluid containing proppant particles coated with a furfuryl alcohol resin composition. The coated proppant particles are deposited in the fractures and the resin coating hardens by heat to consolidate the proppant particles into chemical and thermal degradation resistant permeable packs.

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about 200°F is comprised of the following steps. A liquid hardenable resin composition is provided comprised of furfuryl alcohol resin, furfuryl alcohol, an ethylene glycol butyl ether solvent for the resin, an n-beta-(aminoethyl)-gamma-aminopropyltrimethoxysilane coupling agent, optionally, a mixture of dimethylglutarate, dimethyladipate and dimethylsuccinate esters and a C_{12}-C_{22} alkyl phosphate surfactant. A source of dry proppant particles and a gelled liquid fracturing fluid comprised of water and a gelling agent selected from the group consisting of guar gum, guar gum derivatives and cellulose derivatives are also provided. The gelled liquid fracturing fluid is pumped into the subterranean zone to form the one or more fractures therein and to place the proppant particles therein. The hardenable resin composition is coated onto the dry proppant particles conveyed from the source thereof to form hardenable resin composition coated proppant particles. The hardenable resin composition coated proppant particles are mixed with the fracturing fluid pumped into the subterranean zone whereby the hardenable resin composition coated proppant particles are suspended therein. When the hardenable resin composition coated proppant particles have been placed in the one or more fractures formed in the subterranean zone, the pumping of the gelled fracturing fluid, the coating of the hardenable resin composition onto the dry proppant particles and the mixing of the hardenable resin composition coated proppant particles formed with the fracturing fluid are terminated. Thereafter, the hardenable resin composition on the hardenable resin composition coated proppant particles is allowed to harden by heat and consolidate the proppant particles into one or more chemical and thermal degradation resistant permeable packs.

[0010] The present invention provides improved methods of forming one or more fractures in a subterranean zone penetrated by a well bore and consolidating proppant particles therein, the subterranean zone having a temperature above about 200°F comprising the following steps. Proppant particles coated with a hardenable resin composition comprised of furfuryl alcohol resin, furfuryl alcohol, a solvent for the resin, a silane coupling agent, optionally, a hydrolyzable ester for breaking gelled fracturing fluid films on the proppant particles and a surfactant for facilitating the coating of the resin on the proppant particles and for causing the resin to flow to the contact points between adjacent resin coated proppant particles are provided. A gelled liquid fracturing fluid is also provided. The gelled liquid fracturing fluid is pumped into the subterranean zone to form the one or more fractures and to deposit the proppant particles therein. The proppant particles coated with the hardenable resin composition are mixed with the fracturing fluid pumped into the subterranean zone whereby the proppant particles coated with the hardenable resin composition are suspended therein. When the proppant particles coated with the hardenable resin composition have been deposited in the one or more fractures, the pumping of the gelled liquid fracturing fluid and the mixing of the proppant particles coated with the hardenable resin composition with the fracturing fluid are terminated. Thereafter, the hardenable resin composition on the resin composition coated proppant particles are allowed to harden by heat and consolidate the proppant particles into one or more chemical and thermal degradation resistant permeable packs.

[0011] The proppant particles utilized in accordance with the present invention are generally of a size such that formation particulate solids that migrate with produced fluids are prevented from being produced from the subterranean zone. Various kinds of proppant particles can be utilized including graded sand, bauxite, ceramic materials, glass materials, walnut hulls, polymer beads and the like. Generally, the proppant particles have a size in the range of from about 2 to about 400 mesh, U.S. Sieve Series. The preferred proppant is graded sand having a particle size in the range of from about 10 to about 70 mesh, U.S. Sieve Series. Preferred sand particle size distribution ranges are one or more of 10-20 mesh, 20-40 mesh, 40-60 mesh or 50-70 mesh, depending on the particular size and distribution of formation solids to be screened out by the consolidated proppant particles.

[0012] Furfuryl alcohol resins are readily available from a number of commercial sources. For example, suitable furfuryl alcohol resin is commercially available from Durez Corporation under the trade designation "Durez 33682™". Upon curing by heat in a subterranean zone, the furfuryl alcohol resin forms an insoluble mass that is highly resistant to chemical attack and thermal degradation, i.e., the cured resin resists thermal degradation at temperatures up to 700°F. The furfuryl alcohol resin is generally present in the hardenable resin composition in an amount in the range of from about 40% to about 75% by weight of the composition and more preferably in an amount of from about 55% to about 65%.

[0013] The furfuryl alcohol is generally present in the hardenable resin composition in an amount in the range of from about 1 % to about 20% by weight of the composition and more preferably in an amount of from about 5% to about 15%.

[0014] Examples of solvents for the furfuryl alcohol resin which have flash points above about 125°F and can be utilized include, but are not limited to, dipropylene glycol methyl ether, dipropylene glycol dimethyl ether, diethyleneglycol methyl ether, ethyleneglycol butyl ether, diethyleneglycol butyl ether, dimethyl formamide, propylene carbonate, butyl acetate, furfuryl acetate, d'limonene and fatty acid methyl esters. Of these, ethyleneglycol butyl ether is preferred. The solvent is included in the hardenable resin composition in an amount in the range of from about 10% to about 40% and more preferably in an amount of about 15% to about 30%.

[0015] Examples of silane coupling agents which can be utilized in the hardenable resin composition include, but are not limited to, N-2-(aminoethyl)-3-aminopropyltrimethoxysilane, 3-glycidoxypropyltrimethoxysilane and n-beta-(aminoethyl)-gamma-aminopropyltrimethoxysilane. Of these, n-beta-(aminoethyl)-gamma-aminopropyltrimethoxysilane is

therein.

[0025] The hardenable resin composition of this invention for coating proppant particles and which hardens by heat is basically comprised of a furfuryl alcohol resin, furfuryl alcohol, a solvent for the resin having a flash point above about 125°F, a silane coupling agent, optionally, a hydrolyzable ester for breaking gelled fracturing fluid films and a surfactant for facilitating the coating of the hardenable resin composition on the proppant particles and for causing the hardenable resin composition to flow to the contact points between adjacent resin coated proppant particles.

[0026] The furfuryl alcohol resin, the furfuryl alcohol, the solvent, the silane coupling agent, the hydrolyzable ester and the surfactant are as described above in connection with the methods of this invention and are present in the hardenable resin composition in the amounts set forth above.

[0027] The hardenable resin composition of this invention can be stored at high ambient temperatures for long periods of time without hardening or otherwise deteriorating.

[0028] An improved method of this invention for forming one or more fractures in a subterranean zone penetrated by a well bore and consolidating proppant particles therein, the subterranean zone having a temperature above about 200°F is comprised of the steps of: (a) providing proppant particles coated with a hardenable resin composition comprised of furfuryl alcohol resin, furfuryl alcohol, a solvent for the resin, a silane coupling agent and a surfactant for facilitating the coating of the resin on the proppant particles and for causing the resin to flow to the contact points between adjacent resin coated proppant particles; (b) providing a gelled liquid fracturing fluid; (c) pumping the gelled liquid fracturing fluid into the subterranean zone to form the one or more fractures and to deposit the proppant particles therein; (d) mixing the proppant particles coated with the hardenable resin composition with the fracturing fluid pumped in accordance with step (c) whereby the proppant particles coated with the hardenable resin composition are suspended therein; (e) terminating steps (c) and (d) when the proppant particles coated with the hardenable resin composition have been deposited in the one or more fractures; and; (f) allowing the hardenable resin composition on the resin composition coated proppant particles to harden by heat and consolidate the proppant particles into one or more chemical and thermal degradation resistant permeable packs.

[0029] Another improved method of the present invention for forming one or more fractures in a subterranean zone penetrated by a well bore and consolidating proppant particles therein, the subterranean zone having a temperature above about 200°F is comprised of the steps of: (a) providing a liquid hardenable resin composition comprised of furfuryl alcohol resin, furfuryl alcohol, an ethylene glycol butyl ether solvent for the resin having a flash point above about 125°F, an n-beta-(aminoethyl)-gamma-aminopropyltrimethoxysilane coupling agent and a C_{12}—C_{22} alkyl phosphate surfactant; (b) providing a source of dry proppant particles; (c) providing a gelled liquid fracturing fluid comprised of water and a gelling agent selected from the group consisting of guar gum, guar gum derivatives and cellulose derivatives; (d) pumping the gelled liquid fracturing fluid into the subterranean zone to form the one or more fractures therein and to place the proppant particles therein; (e) coating the hardenable resin composition onto the dry proppant particles conveyed from the source thereof to form hardenable resin composition coated proppant particles; (f) mixing the hardenable resin composition coated proppant particles formed in step (e) with the fracturing fluid pumped in accordance with step (d) whereby the hardenable resin composition coated proppant particles are suspended therein; (g) terminating steps (d), (e) and (f) when the hardenable resin composition coated proppant particles have been placed in the one or more fractures; and (h) allowing the hardenable resin composition on the hardenable resin composition coated proppant particles to harden by heat and consolidate the proppant particles into one or more chemical and thermal degradation resistant permeable packs.

[0030] A hardenable resin composition of this invention for coating proppant particles comprises: a hardenable resin comprised of furfuryl alcohol resin; furfuryl alcohol; a solvent for the resin having a flash point above about 125°F; a silane coupling agent; and a surfactant for facilitating the coating of the hardenable resin composition on the proppant particles and for causing the hardenable resin composition to flow to the contact points between adjacent resin coated proppant particles.

[0031] In order to further illustrate the methods and compositions of this invention, the following examples are given.

Example 1

Effect of Time and Temperature on Viscosity of Mixed Resin

[0032] Furfuryl alcohol resin ("Durez 33682™") obtained from the Durez Corporation was mixed with 1% of a silane coupling agent and 5% of an alkyl phosphate surfactant by weight of the furfuryl alcohol resin. The viscosity of the resin mixture was monitored with time at room temperature and at 120°F in an oven, using a Brookfield DV-II viscometer and spindle No. 3. The temperature of 120°F was selected to simulate the storage temperature in a warehouse during the summer months. Table I shows the recorded viscosities of the resin mixtures at different time periods. The results indicate that the viscosities of the resin mixtures remained substantially unchanged with time, even at higher temperature.

contact points between adjacent resin coated proppant particles.

2. A composition according to claim 1, wherein said furfuryl alcohol resin is present in an amount of from 40% to 75% by weight of said composition.

3. A composition according to claim 1 or 2, wherein said furfuryl alcohol is present in said hardenable resin composition in an amount of from 1% to 20%.

4. A composition according to claim 1, 2, or 3, wherein said solvent for said resin having a flash point above 125°F is dipropylene glycol methyl ether, dipropylene glycol dimethyl ether, dimethyl formamide, diethylene glycol methyl ether, ethylene glycol butyl ether, diethylene glycol butyl ether, propylene carbonate, butyl acetate, furfuryl acetate, d'limonene or a fatty acid methyl esters.

5. A composition according to any of claims 1 to 4, wherein said solvent for said resin having a flash point above 125°F, is present in an amount of from 10% to 40% by weight of said composition.

6. A composition according to any of claims 1 to 5, wherein said silane coupling agent is N-2-(aminoethyl)-3-aminopropyltrimethoxysilane, 3-glycidoxypropyltrimethoxysilane or n-beta-(aminoethyl)-gamma-aminopropyl- trimethoxysilane.

7. A composition according to any of claims 1 to 6, wherein said silane coupling agent is present in said liquid hardenable resin composition in an amount of from 0.1% to 3% by weight of said composition.

8. A composition according to any of claims 1 to 7, which further comprises a hydrolyzable ester for breaking gelled fracturing fluid films on said proppant particles.

9. A composition according to claim 8, wherein said hydrolyzable ester is selected from the group consisting of a mixture of dimethylglutarate, dimethyladipate and dimethylsuccinate, sorbitol, catechol, dimethylthiolate, methyl salicylate, dimethylsuccinate and terbutylhydroperoxide.

10. A composition according to claim 9, wherein said hydrolyzable ester is present in said hardenable resin composition in an amount up to 3%.

11. A composition according to any of claims 1 to 10, wherein said surfactant comprises at least one member selected from ethoxylated nonyl phenol phosphate ester, mixtures of one or more cationic surfactants and one or more non-ionic surfactants and a C_{12}-C_{22} alkyl phosphonate surfactant.

12. A composition according to any of claims 1 to 11, wherein said surfactant is present in an amount of from 1% to 15%, preferably from 4% to 8%, by weight of said composition.

13. A composition according to any of claims 1 to 12, wherein said proppant particles are graded sand.

14. A method of forming one or more fractures in a subterranean zone penetrated by a well bore and consolidating proppant particles therein, the subterranean zone having a temperature above 200°F, which method comprises pumping a gelled liquid fracturing fluid into said subterranean zone, said fluid containing proppant particles coated with a hardenable resin composition suspended therein, to form one or more fractures and to deposit said proppant particles therein; and allowing said hardenable resin composition on said resin composition coated proppant particles to harden by heat and consolidate said proppant particles into one or more chemical and thermal degradation resistant permeable packs; wherein said resin composition is as claimed in any of claims 1 to 13.

15. A method according to claim 14, wherein dry proppant particles have been coated with said resin composition; and wherein said gelled liquid fracturing fluid comprises water and a gelling agent selected from guar gum, guar gum derivatives and cellulose derivatives.

16. A method according to claim 14 or 15, wherein said gelling agent is present in said fracturing fluid in an amount of from 0.2% to 1% by weight of water therein.

17. A method according to claim 14, 15 or 16, wherein said gelled liquid fracturing fluid further comprises a cross-

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